30/585834

WO 2005/073651

*

PCT/FR2005/050011

Cryogenic distillation method and installation for air separation

The present invention relates to a process and to an installation for separating air by cryogenic distillation.

It is known to produce a gas from pressurized air by vaporization of pressurized liquid in an exchange line of an air separation unit by heat exchange with a compressed gas above a cryogenic temperature. Units of this type are known from FR-A-2 688 052, EP-A-0644388, EP-A-1014020 and patent application FR 03/01722.

The energy efficiency of the known units is not excellent as the inflow of heat associated with the cryogenic compression has to be extracted.

In addition, in the case of schemes such as that of figure 7 of US-A-5 475 980, the entire turbine coupled to the cold booster is associated with an energy-absorbing system (oil brake) incorporated onto the shaft of the machines and technologically limited to low power levels (around 70 kW).

25

30

Nevertheless, this type of process does appear to be economically beneficial, in particular when there is little energy reutilization or when energy is available at low cost. It is therefore potentially beneficial to be able to get round the technological limitation of the oil brake integrated onto the shaft of the turbine/booster assembly.

It is an object of the invention to propose an alternative that makes it possible to achieve process schemes based on a cold booster but without an energy dissipation system integrated onto the turbine/booster

shaft, and therefore to envisage using this scheme for practically all sizes of air separation units.

One subject of the present invention is a process for separating air by cryogenic distillation in an installation comprising a double or triple air separation column, the column of which operating at the higher pressure operates at what is called the medium pressure, and an exchange line in which:

- a) all the air is raised to a high pressure, optionally at least 5 bar above the medium pressure, and purified, optionally at this high pressure;
 - b) one portion of the stream of purified air is cooled in the exchange line and is then divided into two fractions;
 - c) each fraction is expanded in a turbine;

15

25

30

35

- d) the intake pressure of the two turbines is (the intake pressures of the two turbines are) at least 5 bar above the medium pressure;
- e) the delivery pressure of at least one of the two turbines is substantially equal to the medium pressure;
 - f) at least one portion of the air expanded in at least one of the turbines is sent to the medium-pressure column of a double or triple column;
 - g) a cold booster mechanically coupled to one of the expansion turbines takes in air, which has undergone cooling in the exchange line, and delivers the air at a temperature above the intake temperature, and the fluid thus compressed is reintroduced into the exchange line in which at least one portion of the fluid undergoes (pseudo) condensation;
 - h) at least one pressurized liquid coming from one of the columns undergoes (pseudo)vaporization in the exchange line at a vaporization temperature, and characterized in that:
 - i) the turbine not coupled to the cold booster is coupled to a booster followed by a cooler; and, optionally,

- ii) the intake temperature of the cold booster is close to the (pseudo)vaporization temperature of the liquid.
- 5 According to other optional aspects of the invention:

•

15

20

25

30

- the installation includes, in addition to the double or triple column, a mixing column, and air coming from at least one of the turbines is sent to the mixing column,
- the air sent to at least one of the turbines upstream of the mixing column comes from the booster other than the cold booster and leaves this booster at a pressure above the high pressure;
 - air coming from at least one of the turbines is sent to the bottom of the mixing column, in order to participate in mass exchange; and
 - air at the high pressure is sent to a bottom reboiler of the mixing column where it at least partially condenses before being sent to the double or triple column.

Another subject of the invention is an installation for separating air by cryogenic distillation, comprising:

- a) a double or triple air separation column, the column of which, operating at the higher pressure, operates at what is called the medium pressure;
 - b) an exchange line;
- c) means for raising all the air to a high pressure, above the medium pressure, and means for purifying it, optionally at this high pressure;
- d) means for sending one portion of the purified air stream into the exchange line in order to cool it and means for dividing this cooled air into two fractions;
- e) two turbines and means for sending one air fraction to each turbine;
 - f) means for sending at least one portion of the air expanded in at least one of the turbines to the medium-pressure column of the double or triple column;

- g) a cold booster, means for sending air, preferably withdrawn from an intermediate point on the main exchange line, to the cold booster and means for sending air boosted in the cold booster into the exchange line at an intermediate point upstream of the withdrawal point;
- h) means for pressurizing at least one liquid coming from one of the columns, means for sending at least one pressurized liquid into the exchange line, and means for expelling a vaporized liquid from the exchange line; and

10

15

25

- i) the cold booster is coupled to one of the turbines,
- characterized in that the turbine not coupled to the cold booster is coupled to an energy dissipation means comprising a booster followed by a cooler.

According to other optional aspects, the installation comprises:

- a mixing column and means for sending air to the mixing column from at least one of the turbines;
 - means for sending one portion of the air compressed in the booster constituting the energy dissipation means, or forming part of the latter, to at least one expansion turbine upstream of the mixing column;
 - means for sending air, coming from at least one of the turbines, into the mixing column in order to participate in mass exchange; and
- means for sending air at the high pressure into a bottom reboiler of the mixing column and means for sending air at least partially condensed in this bottom reboiler to the double or triple column.
- A complementary turbine will be used, operating in parallel with the turbine of the first turbine/booster assembly, and equipped with its own energy dissipation system. Favorably, this system will be a booster followed by a water cooler installed in the warm part.

The expression "close in terms of pressure" means that the pressures differ by at most 5 bar, preferably at most 2 bar. The expression "close in terms of temperature" means that the temperatures differ by at most 15°C, preferably at most 10°C.

A booster is a single-stage compressor.

10 All the pressures mentioned are absolute pressures.

The term "condensation" includes pseudo-condensation. The term "vaporization" includes pseudo-vaporization.

This invention is distinguished from US-A-5 475 980 in that, in figure 4 (optional turbine 9), the two turbines 8, 32 have very different intake pressures, the difference being at least 14 bar, and in figure 5, the pressure difference is about 13 bar and a turbine exhausts at the low pressure, this being prejudicial to the production of pure oxygen.

The invention will be described in greater detail with reference to the figures in which:

- figures 1 and 2 show an air separation unit according to the invention.

30

35

In figure 1, a stream of air at atmospheric pressure is compressed to about 15 bar in a main compressor (not illustrated). The air is then optionally cooled, before being purified (not illustrated) in order to remove the impurities. The purified air is divided into two portions. One portion 3 of the air is sent to a booster 5 where it is compressed to a pressure between 17 and 20 bar, and the boosted air is then cooled by a water cooler 7 before being sent to the warm end of the main exchange line 9 of the air separation unit. The boosted air 11 is cooled down to an intermediate temperature before leaving the exchange line and being divided into

fractions. Of course, it is possible that a two fraction of the stream 11 continues to be cooled until reaching the cold end of the exchange line 9, from where it will emerge liquefied. A fraction 13 is sent to a turbine 17 and the remainder - a fraction 15 - is sent to a turbine 19. The two turbines have the same intake temperature and pressure and the same discharge temperature and pressure, but of course it is possible for these temperatures and pressures to be close to one another instead of being identical. The two streams output by the turbines are mixed together to form a stream 21 of air, a portion 121 of which is sent to the double column and the remainder - a portion 122 - is sent to the mixing column 300. The stream 122 constitutes one portion of the stream 21 or optionally a fraction of the gaseous portion of the stream 21 in the case in which the latter is a two-phase stream. Of course, it is possible to send the entire stream 21 to medium-pressure 100 column and withdraw to therefrom a gaseous portion 122 to be sent to the mixing column, the medium-pressure column in this case replacing the phase separator. The pressures of the medium-pressure column and the mixing column may be different. As a variant, the turbine 19 may be a blowing turbine delivering at the pressure of the lowpressure column.

Another portion 2 of the air at 15 bar, constituting the remainder of the feed air, is cooled in the exchange line to an intermediate temperature above the intake temperature of the turbines 17, 19, compressed in a second booster 23 up to about 30 bar and reintroduced into the exchange line 9 at a higher temperature so as to continue its cooling.

35

5

10

15

20

25

30

Thus, the air 37 at about 30 bar liquefies in the exchange line and liquid oxygen 25 vaporizes in the exchange line, the vaporization temperature of the liquid being close to the intake temperature of the

second booster 23. The liquefied air leaves the exchange line and is sent to the column system.

A waste nitrogen stream 27 is warmed in the exchange line 9.

The first booster 5 is coupled to one of the turbines, 17 or 19, and the second booster 23 is coupled with the other of the turbines, 19 or 17.

10

15

The column system of an air separation unit is formed by a medium-pressure column 100 thermally coupled with a low-pressure column 200 having a minaret, a mixing column 300, and an optional argon column (not illustrated). The low-pressure column does not necessarily have a minaret.

The medium-pressure column operates at a pressure of 5.5 bar, but it may operate at a higher pressure.

20

The air 121 coming from the two turbines 17, 19 is the stream sent into the bottom of the medium-pressure column 100.

The liquefied air 37 is expanded in the valve 39 or, optionally, in a turbine, and sent to the column system.

Rich liquid 51, lower lean liquid 53 and upper lean liquid 55 are sent from the medium-pressure column 100 to the low-pressure column 200 after in-valve expansion and subcooling steps.

Liquid oxygen is pressurized by the pump 500 and sent as pressurized liquid 25 to the exchange line 9. Other liquids, whether pressurized or not, may be vaporized in the exchange line.

Optionally, gaseous nitrogen is withdrawn from the medium-pressure column and is cooled, again in the exchange line 9.

5 Nitrogen 33 is withdrawn from the top of the lowpressure column and warmed in the exchange line, after having served for subcooling the reflux liquids.

Waste nitrogen 27 is withdrawn from a lower level of the low-pressure column and warmed in the exchange line, after having served for subcooling the reflux liquids.

Optionally, the column may produce argon, by treating a stream 51 withdrawn into the low-pressure column 200. The stream 52 is the bottoms liquid sent from the argon column, if there is one.

The mixing column 300 is fed at the top with an oxygenrich liquid 35, withdrawn from an intermediate level of
the low-pressure column 200 and pressurized by the pump
600, and at the bottom with a stream 122 of gaseous air
coming from the turbines 17, 19. The mixing column
essentially operates at the medium pressure.

25

30

A gaseous oxygen stream 37 is withdrawn from the top of the mixing column and then warmed in the exchange line 9, and a liquid stream 41 is withdrawn as bottoms and sent to the low-pressure column after being expanded in a valve. It is possible to withdraw an intermediate stream from the column 300, which is sent to the low-pressure column.

In figure 2, a stream of air at atmospheric pressure is compressed to about 15 bar in a main compressor (not illustrated). The air is then optionally cooled, before being purified (not illustrated) in order to remove the impurities. The purified air is divided into two portions. One portion 3 of the air is sent to a booster

5 where it is compressed to a pressure of between 17 and 20 bar, and then the boosted air is cooled by a water cooler 7 before being sent to the warm end of the main exchange line 9 of the air separation unit. The boosted air 11 is cooled down to an intermediate temperature before being divided into two fractions 103, 123. The fraction 103 leaves the exchange line and is again divided into two fractions. One fraction 13 is sent to a turbine 17 and the remainder - a fraction 15 - is sent to a turbine 19. The two turbines have the 10 intake temperature and pressure and the same discharge temperature and pressure, but it is of course possible for these temperatures and pressures to be close to one another instead of being identical. The two streams output by the turbines are mixed together 15 to form a stream 21 of air, one portion 121 of which is sent to the double column and the remainder - a portion 122 - is sent to the mixing column 300. As a variant, the turbine 19 may be a blowing turbine delivering at the pressure of the low-pressure column. 20

The fraction 123 continues to be cooled in the exchange line 9 and exits therefrom upstream of the cold end to be sent to the bottom reboiler 301 of the mixing column 300, where the fraction condenses, at least partially, in order to form the stream 125.

Another portion 2 of the air at 15 bar, constituting the remainder of the feed air, is cooled in the exchange line down to an intermediate temperature above the intake temperature of the turbines 17, 19, compressed in a second booster 23 to about 30 bar and reintroduced into the exchange line 9 at a higher temperature, so as to continue its cooling.

35

25

30

Thus, the air 37 at about 30 bar is liquefied in the exchange line and liquid oxygen 25 is vaporized in the exchange line, the vaporization temperature of the liquid being close to the intake temperature of the

second booster 23. The liquefied air leaves the exchange line and is sent to the column system after being mixed with the liquefied air 125 coming from the reboiler 301.

5

A waste nitrogen stream 27 is warmed in the exchange line 9.

The first booster 5 is coupled with one of the turbines, 17 or 19, and the second booster 23 is coupled with the other of the turbines, 19 or 17.

The column system of an air separation unit is formed by a medium-pressure column 100 thermally coupled with a low-pressure column 200 having a minaret, a mixing column 300, and an optional argon column (not illustrated). The low-pressure column does not necessarily have a minaret.

The medium-pressure column operates at a pressure of 5.5 bar, but it may operate at a higher pressure.

The gaseous air 21 coming from the two turbines 17, 19 is the stream sent to the bottom of the medium-pressure column 100.

The liquefied air 37 is expanded in the valve 39 and sent at least to the medium-pressure column 100.

- 30 Rich liquid 51, lower lean liquid 53 and upper lean liquid 55 are sent from the medium-pressure column 100 to the low-pressure column 200 after in-valve expansion and subcooling steps.
- Liquid oxygen is pressurized by the pump 500 and sent as pressurized liquid 25 to the exchange line 9. In addition or alternatively, other liquids, whether pressurized or not, may be vaporized in the exchange line.

Gaseous nitrogen is optionally withdrawn from the medium-pressure column and is cooled, again in the exchange line 9.

5 .

Nitrogen 33 is withdrawn from the top of the lowpressure column and is warmed in the exchange line, after having served to subcool the reflux liquids.

- Waste nitrogen 27 is withdrawn from a lower level of the low-pressure column and warmed in the exchange line, after having served to subcool the reflux liquids.
- Optionally, the column may produce argon, by treating a stream 51 withdrawn into the low-pressure column 200.

The mixing column 300 is fed only at the top with an oxygen-rich liquid 35 withdrawn from an intermediate level of the low-pressure column 200 and pressurized in the pump 600. The mixing column operates essentially at the medium pressure. By modifying the pressure of the stream 123, the mixing column 300 may operate at a pressure different from the medium pressure.

25 Optionally, one portion of the rich liquid 51 may be

sent to the bottom of the column 300.

A gaseous oxygen stream 37 is withdrawn from the top of the mixing column and warmed in the exchange line 9, 30 and a liquid stream 41 is withdrawn as bottoms and sent to the low-pressure column after being expanded in a valve.